

PATENT SPECIFICATION

(11) 1 546 633

1546633 (21) Application No. 22097/76 (22) Filed 27 May 1976
 (31) Convention Application No. 580 845
 (32) Filed 27 May 1975 in
 (33) United States of America (US)
 (44) Complete Specification published 31 May 1979
 (51) INT CL² G03C 1/52
 (52) Index at acceptance

G2C 1B3A 1B3B 1E1B 1G1 1G5 C4A C4C5C
 (72) Inventors RONALD HENRY ENGBRECHT and JOHN
 RAYMOND GUILD



(19)

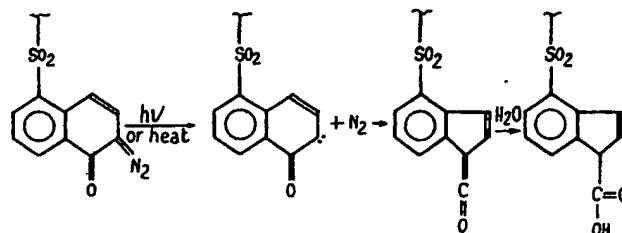
(54) PHOTORESIST COATING COMPOSITIONS

(71) We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to coating compositions for preparing presensitised plates used in the graphic arts to produce photomechanical images such as photoresists and lithographic plates.

10 Although the literature relating to the decomposition of quinone diazides in positive-working photoresist compositions is extensive, the exact structure of the decomposition product is not certain. Equation 1 is at least representative of the reasons for solubilization of said compositions upon exposure.

Equation 1



15 Loss of nitrogen to form the ketocarbene is the expected initial step; however, the fate of the ketocarbene is less predictable. One documented reaction sequence is the rearrangement to ketene followed by hydrolysis to free acid. Due to the immobility of a dry film, the formation of ketene via intramolecular rearrangement is expected; however, alternative reactions before hydrolysis have been reported.

20 The evolution of nitrogen during the storage of compositions containing o-quinone diazides such as coating compositions can adversely affect the safe storage of such materials. Such materials can become a safety hazard if they are stored in sealed containers at temperatures above 100°F for extended periods of time.

25 US Patent 3 046 120 (UK 711 626) discloses in claim 1 presensitised printing plates comprising a base material having a coating thereon comprising the condensation product of a sulphonic acid halide of a quinone-(1,2)-diazide and a phenol-formaldehyde resin. The product of the condensation is described as a water-insoluble resin-like ester. The light-sensitive layer is advantageously produced on the base by dissolving the resin-like ester in an organic solvent or solvent mixture and applying the solution to the base and drying.

30 US Patent 4 036 644, on which is based German OLS 2 410 880 published in the UK on the 19 September 1974, discloses an article having a silicon substrate having a surface coating of silicon oxide, phosphosilicate glass, sputtered quartz or metal coated with a layer of resist consisting essentially of a novolak polymer, light-sensitive diazo ketone compound of formula:

1

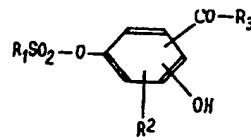
15

20

25

30

35



in which R₁ is a naphthoquinone-(1,2)-diazide radical, R₂ is selected from the group consisting of hydrogen and hydroxyl, and R₃ is selected from the group consisting of hydrogen, alkyl, acyl, alkoxy, acyloxy, amino and heterocyclic groups, in proportions of between about 1:1 and 1:6 by weight of diazo ketone of novolak polymer, and from about 1 to 11% by weight based on resist solids of an aliphatic carboxylic acid containing from about 3 to 30 carbon atoms.

The results are applied to substrates from solvent mixtures. In Example 1 the coated substrate is baked.

US patents 3 046 110, 3 046 112, 3 046 113, 3 046 116 and 3 046 118 disclose the incorporation of small amounts of solid, non-volatile fatty acids into light-sensitive compositions to improve ink receptivity and stability. Although the addition of non-volatile carboxylic acids (e.g. fatty acids) to photoresist compositions does reduce the rate of nitrogen formation from quinone diazide decompositions, we have found that the presence of the non-volatile acids causes unacceptable image degradation during processing of the dried resist layer.

We have now found that the incorporation of certain volatile aliphatic carboxylic acids in a coating composition containing the condensation product of an acidic quinone diazide derivative and a phenol-aldehyde resin at least substantially reduces the evolution of nitrogen from the composition on storage and that it is advantageous to remove the volatile acid from the coated layer before use.

According to the present invention there is provided a coating composition for preparing a presensitised plate comprising:

A a light-sensitive polymeric compound formed from the condensation reaction of an acidic quinone diazide derivative with a phenol-aldehyde resin;

B a volatile carboxylic acid which has the formula:



wherein R is H, an alkyl group having 1 to 3 carbon atoms, an alkoxy group having 1 to 3 carbon atoms or a cyano, halo or nitro group and m is an integer from 0 to 4, and which has a boiling point equal to or less than 200°C at atmospheric pressure; and

C a coating solvent.

The coating composition of this invention may be used to make a photosensitive element by coating a support with a layer of the composition and evaporating the volatile carboxylic acid and coating solvent therefrom.

A photomechanical image may be prepared from the photosensitive element by exposing the element to actinic radiation so that the quinone diazide structure is decomposed rendering the exposed areas of the photosensitive layer soluble in dilute alkali. A positive image is developed by removing the exposed areas of the layer with an aqueous alkaline developer.

The use of a volatile carboxylic acid in the coating compositions of the invention increases the safe storage life of said compositions.

In the present invention the volatile carboxylic acid used has the formula



wherein R is hydrogen, a lower alkyl, a lower alkoxy, a cyano, a halo or nitro group and m is an integer from 0 to 4, preferably 0 to 2.

For purposes of this invention a lower alkyl is one having from 1 to 3 carbon atoms, e.g. methyl, ethyl, propyl; a lower alkoxy is one having from 1 to 3 carbon atoms, e.g., methoxy, ethoxy, propoxy, and a halo group represents a substituent such as bromide, chloride, fluoride or iodide.

The volatile carboxylic acids used in this invention also have boiling points equal to or below 200°C at atmospheric pressure. Some of the acids useful in the present invention are listed in Table I below with their respective boiling and melting points.

TABLE I
Volatile Carboxylic Acids*

	m.p. °C (760 mmHg)	b.p. °C (760 mmHg)
Formic Acid	8	100.5
Acetic Acid	16.6	118
Propionic Acid	-22	141
Butyric Acid	-6	164
Valeric Acid	-34	187

*Morrison and Boyd, Organic Chemistry, 2nd Ed., 1966, Page 579

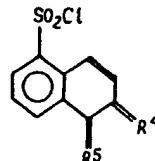
Although the amount of volatile carboxylic acid used can vary widely, the concentration of the volatile carboxylic acid in the coating compositions of the invention is preferably within the range of 1 to 50 percent by weight based on the total solids of said composition, and more preferably within the range of 1 to 20 percent by weight.

The following patents review the preparation and application of light-sensitive phenol-formaldehyde polymers containing quinone diazide substituents: U.S. Patent 3,046,120, U.K. Patents 1,026,144 and 1,113,759; German Patents 1,803,712 and 1,911,497; and Canadian Patent 903,545.

The coating compositions and elements of the invention comprise a light sensitive polymeric compound formed by the condensation reaction of an acidic quinone diazide derivative with a phenolformaldehyde resin. Preferably, the acidic quinone diazide derivative used in forming the photosensitive polymer forms with the phenol-formaldehyde resin a linkage selected from sulphonyl

(---S---), carbonyl (---C=O---), carbonyloxy (---C(=O)O---), and sulphonyloxy (---S(=O)---O---).

The most preferred acidic quinone diazide derivative is 1,2-naphthoquinone-1- or 2-diazide-5-sulphonyl chloride, having the formula



wherein R^4 and R^5 are interchangeably N, or O, and R^4 and R^5 are not the same.

Other quinone diazide derivatives useful in the practice of this invention are the acid esters and acid halides of o - benzoquinone diazide, 1,2 - naphthoquinone-1 - diazide, 7 - methoxy - 1,2 - naphthoquinone - 2 - diazide, 6 - chloro - 1,2 - naphthoquinone - 2 - diazide, 7 - chloro - 1,2 - naphthoquinone - 2 - diazide, 6 - nitro - 1,2 - naphthoquinone - 2 - diazide, 5 - (carboxymethyl) - 1,2 - naphthoquinone - 1 - diazide, 3,3',4,4' - diphenyl - bis - quinone - 4,4' - diazide, 2,3 - phenanthrenequinone - 2 - diazide, 9,10 - phenanthrenequinone - 10 - diazide and 3,4 - chrysenequinone - 3 - diazide, and other such quinone diazides substituted with such groups as alkyl having one to eight carbon atoms, e.g., methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl and octyl; alkoxy having 1 to 8 carbon atoms, e.g. methoxy, ethoxy, propoxy, butoxy, amyoxy, hexyloxy, heptyloxy and octyloxy; and other groups which do not interfere with the photosensitive properties of the quinone diazide.

The phenol-formaldehyde resins used in the practice of this invention, such as novolak or resole resins, are described in Chapter XV of "Synthetic Resins in Coatings", H. P. Preuss, Noyes Development Corporation (1965), Pearl River, New York.

The novolak resins are prepared by the condensation of phenols and aldehydes under acidic conditions whereas the resole resins are prepared under basic conditions.

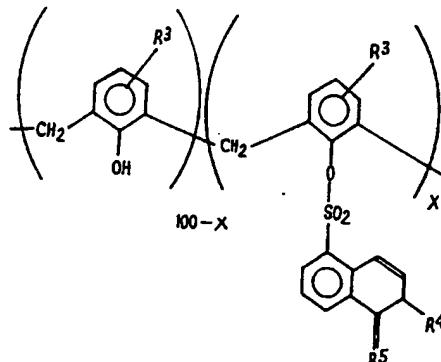
Less than 6 moles of aldehyde are used per 7 moles of phenol to provide products which are permanently fusible and soluble. In a typical synthesis, novolaks are prepared by heating 1 mole of a phenol with 0.5 mole of an aldehyde under acidic conditions. The temperatures at which the reaction is conducted are generally from 25°C to 175°C.

10 These resins are prepared by the condensation of a phenol with an aldehyde, more generally by the reaction of a phenolic compound having two or three reactive aromatic ring hydrogen positions with an aldehyde or aldehyde-liberating compound capable of undergoing phenol-aldehyde condensation. Illustrative of particularly useful phenolic compounds are cresol, xylene, ethylphenol, butylphenol, isopropylmethoxyphenol, chlorophenol, resorcinol, hydroquinone, naphthol and 2,2-bis(hydroxyphenyl)-propane. Illustrative of especially efficacious aldehydes are formaldehyde, acetaldehyde, acrolein, crotonaldehyde and furfural. Illustrative of aldehyde-liberating compounds 1,3,5-trioxane.

15 The most suitable phenolic resins are those which are insoluble in water and trichloroethylene but readily soluble in conventional organic solvents such as methyl ethyl ketone, acetone, methanol and ethanol. Phenolic resins having a particularly desirable combination of properties are those which have an average molecular weight in the range between 350 and 40,000, and preferably in the range between 350 and 2000.

Preferred phenol-aldehyde resins are cresol-formaldehyde and phenol-formaldehyde.

In a preferred embodiment of this invention, the light sensitive polymer employed is a compound having the formula



25

25

wherein R³ is hydrogen or methyl; R⁴ and R⁵ are interchangeably N₂ or O, but not the same; and X is from 1 to 99 mole percent. We have found, however, that acceptable imaging properties in short development times are obtained when X is from 1 to 50 mole percent, and best results when X is from 4 to 20 mole percent.

30 to 50 mole percent, and best results when X is from 4 to 20 mole percent.
35 The light sensitive polymeric compounds useful in the present invention are
preferably prepared from condensation reactions of a suitable acidic quinone diazide
derivative (e.g. one of those listed above) with a suitable phenol-aldehyde resin.
These reactions are usually carried out in an organic medium, such as dioxane, tetra-
hydrofuran or acetone, where the concentration of the reactive compounds is in the
range of 1 to 50 percent of the solution weight; at a temperature in the range of 0°C
to 78°C and at various pressures, preferably atmospheric pressure. The molar ratio
of acidic quinone diazide compound to phenol-aldehyde resin may be in the range
of 99:1 to 1:99 and preferably from 1:25 to 1:5. The resulting quinone diazide
phenol-aldehyde polymer can be collected by precipitation of the reaction product
in a dilute acid, such as hydrochloric acid and filtering.

In another preferred embodiment of the present invention, the coating compositions and elements further comprise a non-light sensitive film forming polymer wherein the weight ratio of light sensitive polymer to non-light sensitive polymer is in the range of 1:1 to 99:1. As the amount of acidic quinone diazide compound used in a photosensitive composition is increased the amount of non-light sensitive polymer may be increased.

The non-light sensitive polymers are addition homopolymers or interpolymers formed by the addition polymerization of one or more unsaturated compounds containing the unit $>C=C<$ and generally having a molecular weight in the range of

2000 to 50,000, although they can have higher or lower molecular weights for particular applications.

5 Unsaturated compounds which can be homopolymerized or interpolymerized and used as non-light sensitive polymeric materials include vinyl amines, vinyl imines, substituted and unsubstituted styrenes, acrylates and methacrylates such as alkyl acrylates and alkylmethacrylates, vinyl halides, vinyl esters, vinyl ethers, vinyl ketones, divinyl ethers, acrylonitrile, mixed esteramides and maleic anhydride, 1,3-butadiene, isoprene, chloroprene, divinylbenzene and acrylic and methacrylic acid derivatives such as nitriles and amides.

10 10 Interpolymers and homopolymers can be prepared by any suitable method including addition polymerization, for example, bulk, solution, bead and emulsion polymerization methods in the presence of a polymerization initiator. For example, polymerization of aminostyrene is conveniently carried out by contacting a mixture of aminostyrene and another polymerizable ethylenically unsaturated compound with 15 from 0.1% to 10%, preferably 0.2 to 2%, of a free radical liberating polymerization initiator.

20 Examples of suitable initiators are peroxy compounds, for example, benzoyl peroxide or di(tertiary amyl)peroxide and azo initiators, for example, 1,1' - azo-dicyclohexanecarbonitrile or azodiisobutyronitrile. The polymerization can be carried out in the presence or absence of an inert solvent such as a hydrocarbon, for example, benzene, white mineral oil, or lubricating oil, acetic acid and dioxane, and preferably in an inert atmosphere, for example, under a blanket of nitrogen. The mixture is maintained at a temperature at which the polymerization initiator generates free radicals rapidly. The exact temperature selected depends on the particular initiator being used. Temperatures ranging from room temperature or lower up to 150°C. 25 or higher are suitable. It is usually desirable to carry the polymerization substantially to completeness so that no unpolymerized monomer remains and the proportions of each component in the final product are essentially those of the original monomer mixture.

30 Other non-light sensitive polymers suitable for use in the present invention are film forming condensation resins, such as phenol formaldehyde resins.

35 Coating compositions of the invention can be prepared by forming a solution of the light sensitive polymeric compound alone or mixed with a film forming non-light sensitive material. These compositions can then be used to form resists or lithographic plates.

40 The solvents which can be employed as coating solvents in preparing coating compositions of the invention are preferably organic solvents which may be selected from those which are capable of dissolving at least 0.2% by weight of the light sensitive materials employed but are unreactive toward the light sensitive materials and which are substantially incapable of attacking the substrates employed. Exemplary solvents include dimethylformamide, cyclohexane, cyclohexanone, acetonitrile, 2-ethoxyethanol, acetone, 4-butyrolactone ethylene glycol monomethyl ether acetate, 2-methoxyethyl acetate, butyl acetate, and mixtures of these solvents with each other or with one or more of the lower alcohols and/or ketones.

45 The concentration of light sensitive polymer in the coating solutions is dependent upon the nature of the light sensitive materials, the supports and the coating methods employed. Particularly useful coatings are obtained when the coating solutions contain from about 0.05 to 25 percent by weight of light-sensitive material.

50 It will be recognized that additional components can be included in the coating compositions of the present invention. For example, dyes and/or pigments can be included to obtain colored images; resins, stabilizers and surface active agents may serve to improve film formation, coating properties, adhesion of the coatings to the supports employed, mechanical strength and chemical resistance.

55 Photosensitive elements bearing layers of the polymeric materials disclosed herein can be prepared by coating the coating compositions of the invention onto supports in accordance with usual practices. Suitable support materials include fibre base materials such as paper, polyethylene-coated paper, polypropylene-coated paper, parchment and cloth; sheets and foils of such metals as aluminium, copper, magnesium and zinc; glass and glass coated with such metals as chromium, chromium alloys, steel, silver, gold, and platinum; synthetic polymeric materials such as poly(alkyl methacrylates), e.g., poly(methyl methacrylate), polyester film base, e.g., poly(ethylene terephthalate), poly(vinyl acetals), polyamides, e.g., nylon, cellulose ester film base, e.g., cellulose nitrate, cellulose acetate, cellulose acetate propionate, and cellulose acetate butyrate. The supports especially polymeric supports such as poly-

(ethylene terephthalate), can be subcoated with materials which aid adhesion to the support. A preferred class of subcoatings is polymers, copolymers and terpolymers of vinylidene chloride alone or with acrylic monomers such as acrylonitrile, and methyl acrylate, and unsaturated dicarboxylic acids such as itaconic acid. The support can also carry a filter or antihalation layer composed of a dyed polymer layer which absorbs the exposing radiation after it passes through the light-sensitive layer and eliminates unwanted reflection from the support. A yellow dye in a polymeric binder, such as one of the polymers referred to above as suitable subcoatings, is an especially effective antihalation layer when ultraviolet radiation is employed as the exposing radiation. The optimum coating thickness of the light sensitive layer will depend upon such factors as the use to which the coating will be put, the particular light sensitive polymer employed, and the nature of other components which may be present in the coating. Typical coating thicknesses for use in preparing resists are from 0.1 to 0.5 mils.

15 The photographic elements prepared from the coating compositions of the present invention can be imagewise exposed by conventional methods to a source of actinic radiation which is preferably a source which is rich in ultraviolet light. Suitable sources include carbon arc lamps, mercury vapour lamps, fluorescent lamps, tungsten filament lamps, lasers, and the like. The exposed elements can then be developed by flushing, soaking, swabbing, or otherwise treating the light sensitive layers with a solvent or solvent system which exhibits a differential solvating action on the exposed and unexposed areas. The exposed areas of the coating will be removed by the solvent while the unexposed areas will be unaffected. These developing solvents may be organic or aqueous in nature and will vary with the composition of the photographic layer to be developed. Exemplary solvents include water, aqueous alkali, the lower alcohols and ketones, and aqueous solutions of the lower alcohols and ketones. The resulting images may then be treated in any known manner consistent with their intended use such as treatment with desensitizing etches and plate lacquers.

30 A preferred process for forming and treating the element comprises applying the photoresist solution to a clean surface to be etched by spraying, dipping, and whirling, and then air drying. If desired, a prebake of 10 to 15 minutes at 80°C is given to remove residual solvent and the coating is exposed through a pattern to a light source. The resist coating, is then placed in a developer solvent such as an aqueous alkaline developer, to remove the exposed areas. The developer can also contain dyes and/or pigments and hardening agents. The developed image is rinsed with distilled water, dried and optionally postbaked for 15 to 30 minutes at 80°C to 120°C. The substrate can then be etched by acid etching solutions such as ferric chloride.

35

40 The following preparations are included to illustrate the production of materials useful in the practice of the invention:

Preparation 1:

Esterification of Alnovol 429K Resin* with 1,2-naphthaquinone-2-diazide-5-sulphonyl chloride (NDS-Cl).

45 Six grams (50 millimoles) of Alnovol 429K Resin* were dissolved in 50 ml of dioxane and were added to 10% excess 1,2 - naphthaquinone - 2 - diazide - 5-
50 sulphonyl chloride (NDS-Cl) (15 g, 55 millimoles) dissolved in 100 ml of dioxane. As the solution was stirred, a 33% solution of triethylamine (7.5 g, 75 millimoles) in dioxane was added dropwise. After stirring for three hours, distilled water was added (15 ml) to dissolve a gummy precipitate which had formed during the reaction. This fraction is believed to be aminehydrochloride and a high molecular weight polymer.

The gummy precipitate was kept in solution during the reaction by the addition of small amounts of distilled water until the solution cleared followed by continued amine addition. This procedure was repeated until all the amine had been added.

55 The solution was then precipitated in 4 litres of 0.1% hydrochloric acid, filtered, washed with distilled water, and air dried at 40°C. for 16 hours to yield fully esterified polymer. The polymer yielded an infrared spectrum with the expected absorption peaks at 2,183 and 2,119 cm^{-1} (indicating the presence of the



group) and a reduced absorption peak (associated with a phenolic OH group) at 3,333 cm^{-1} . (See Table II).

*Alnovol 429K is a cresol formaldehyde resin produced by Chemische Werke Albert, Wiesbaden-Biebrich and sold by American Hoechst Corp., North Somerville, New Jersey.

5

Preparation 2:

Esterification of Durite* S-3937 resin with NDS-Cl

Several samples of Durite* S-3937 resin were esterified with 1,2 - naphthaquinone - 2 - diazide - 5 - sulphonyl chloride to 100%, 70%, 60%, 50% and 30% of available reactive phenol groups, respectively. The procedures used were similar to that described in Preparation 1 (See Table II).

10

1C

*Durite S-3937 is a phenol-formaldehyde resin prepared by Borden Chemical Division.

1C

Preparation 3:

Low NDS-Cl Esterification of Cresol Novolak Resins

1C

Twelve grams (100 millimoles) of a cresol novolak resin were dissolved in 100 ml of dioxane and added to a solution of 1,2 - naphthaquinone - 2 - diazide - 5 - sulphonyl chloride (2.7 g, 10 millimoles) dissolved in 100 ml of dioxane. The mixture was placed in a 500 ml, three-neck, round-bottom flask fitted with an electric stirrer and a separating funnel. The reaction flask was chilled in a water bath to 10°C. As the solution was stirred, triethylamine (2.0 g, 20 millimoles) dissolved in 30 ml of dioxane was added dropwise.

2C

The reaction was allowed to proceed for 2 hours during which time a gummy precipitate separated. The reaction solution was filtered and the supernatant liquid precipitated in 4 litres of 0.1% hydrochloric acid. The resulting product was suction filtered, washed with distilled water, and air dried at 40°C. for 16 hours. The light yellow product yielded an infrared spectrum similar to the polymer prepared in Preparation 1. Approximately 10% of the cresol-novolak was esterified (Table II).

2C

2C

Preparation 4:

A Micropositive Photoresist Element Containing Polymers with High NDS-Cl Content

3C

Photoresist Composition

1 g Light-sensitive polymer FF (Table II)

3C

3 g Alnovol 429K

17 g Cyclohexanone

3C

The above resist was coated on silicon dioxide wafers at 4500 rpm to give a resist film of 6000 to 8000 Å thickness. The coated wafers were prebaked for 20 minutes at 80°C, exposed for 10 seconds to a colight "Exposer I" (mercury vapour) light source, and developed for 2.5 minutes in a developer comprising:

4C

10 ml 2-ethoxyethanol

4C

7 ml a nonyl phenoxy-polyglycol (Olin Surfactant 10G)

27 ml distilled water.

Lines or spaces of less than 2 microns were resolved. After etching the silicon dioxide to a depth of 8000 Å in a buffered hydrofluoric acid solution, all original lines of 3 microns or wider were retained.

4C

The other high percent NDS-Cl esterified light-sensitive polymers AA through JJ from Table II were subsequently examined via the procedure of Preparation 4, and all produced images. Variations in image quality were observed and different exposure and development times were required.

4C

As the NDS-Cl content of the Novolak polymer was increased from 50% to 100% of the available reactive sites on the phenol-formaldehyde resin, poorer quality images, longer development times and some attack of the image edges were observed. Optimum results were obtained with polymers having from about 5% to 10% NDS-Cl content.

5C

TABLE II
NDS Sulphonated Polymers Prepared as in Preparations 1 through 3

Light Sensitive Polymer	Theoretical % NDS-Cl	Novolak Polymer
AA	100	Alnovol 429K
BB	50	Alnovol 429K
CC	100	Durite S-3937
DD	70	Durite S-3937
EE	60	Durite S-3937
FF	50	Durite S-3937
GG	40	Durite S-3937
HH	30	Durite S-3937
II	50	Cresol Novolak (low mol. wt.)
JJ	40	Cresol Novolak (low mol. wt.)
KK	10	Cresol Novolak (low mol. wt.)
LL	7.5	Cresol Novolak (low mol. wt.)
MM	5	Cresol Novolak (low mol. wt.)
NN	10	Cresol Novolak (high mol. wt.)
OO	6	Cresol Novolak (high mol. wt.)

A volatile acid can be added to the above described photosensitive compositions in accordance with this invention.

Preparation 5:

Poly(ethyl acrylate-co-methacrylic acid) Non-Light Sensitive Polymer for Photoresist Formulations

The following reagents were placed in a three litre, three-neck flask equipped with a nitrogen inlet tube, and a water-jacketed condenser fitted with a constricted outlet to reduce air backflow into the flask.

1440 g 2-ethoxyethyl acetate

144 g ethyl acrylate

16 g methacrylic acid

1.6 g 2,2'-azobis(2-methylpropionitrile) recrystallized from methanol

The reaction was flushed with nitrogen for one hour and subsequently immersed in a 90°C water bath for 16 hours. The flow of nitrogen was continued during the polymerization.

No isolation of the resulting polymer was required. The polymer/solvent mixture can be used directly in the preparation of a micropositive resist.

Analysis of the resulting polymer gave the following data:

20 Number Ave. Mol. Wt. 7,600 20
Weight Ave. Mol. Wt. 14,100

Examples 1-4:

The Rate of Thermal Degradation of a Micropositive Photoresist Formulation Containing Two o-Quinonediazide Polymers

25 2.4 g Acryloid AT-75 (non-light sensitive polymer made by Rohm and Haas)

1.8 g light sensitive polymer* (i)

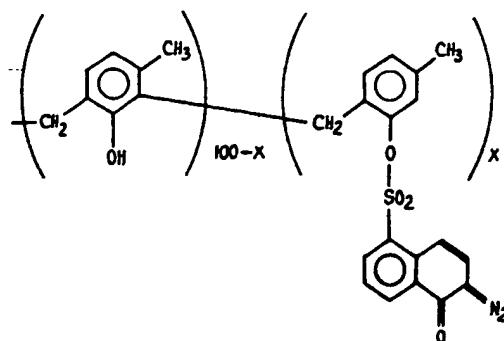
1.8 g light sensitive polymer* (ii)

6.9 g 2-methoxyethyl acetate

6.9 g butyl acetate

25

* The light sensitive polymers (i) and (ii) are m-cresol novolak resins of molecular weights 1500 to 2500 having the formula



in which X is 10 mole percent and 5 mole percent respectively.

Acryloid AT-75 is a commercial non-light sensitive polymer of poly(acrylic acid-co-ethyl acrylate) used as a binder.

This photoresist formulation was placed in a stainless steel container fitted with a 30 lb/in² (1550 mmHg) pressure gauge which was filled to 92% of capacity with this positive photoresist formulation and stored at 44°C. The rate of pressure build-up from released nitrogen gas is recorded in Table III in the 'Control' line.

The above described photoresist formulation was modified by the addition of various amounts of volatile acids in weight percent based on weight of total solids. Each photoresist was placed in a stainless steel container and stored at 44°C as for the 'Control'. The rates of pressure build-up from released nitrogen gas are recorded in Table III.

TABLE III

Example	Volatile Acid wt/%	Pressure at 44°C (mm Hg)			Thermal Stability
		9 days	2 weeks	3 weeks	
Control	none	105	360	725	poor
1	2.5% glacial acetic acid	13	105	270	excellent
2	7.5% glacial acetic acid	39	130	310	excellent
3	2.5% formic acid	26	130	310	excellent
4	2.5% propionic acid	65	155	350	excellent

In determining thermal stability, a pressure build-up of less than 365 mmHg over a period of three weeks at 44°C is considered to be an indication of excellent stability for long term storage of positive resist formulations.

The most preferred embodiments of this invention are shown in Examples 1-4 wherein formic acid, acetic acid and propionic acid are used to give excellent results in all properties.

The following Example describes one embodiment of the lithographic plate of the invention.

Example 5.

A lithographic plate was prepared by coating on to a 6 mil anodized aluminium support a photosensitive composition comprising 180 gm of the NDS-Cl novolak condensation product MM described in Preparation 4, 500 grams of the acrylic binder of Preparation 5, 6 grams of glacial acetic acid and 0.9 grams of Sudan IV dye at a coverage of 200 mg/ft². The coating was dried under a coating drum at a temperature of 80°F in a forced air cabinet at 134°F.

The element was exposed for 2 minutes to a carbon arc source and developed by swabbing for 1 minute with a sodium phosphate (tribasic) with sodium silicate developer. The lithographic plate was capable of making more than 10,000 impressions.

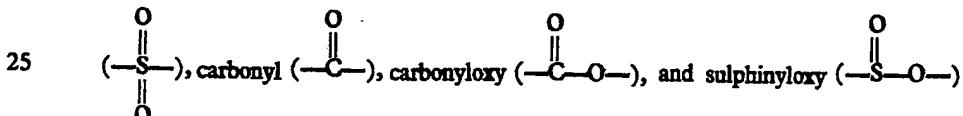
WHAT WE CLAIM IS:—

1. A coating composition for preparing a presensitised plate comprising:
 A a light-sensitive polymeric compound formed from the condensation reaction
 of an acidic quinone diazide derivative with a phenol-aldehyde resin;
 5 B a volatile carboxylic acid which has the formula:



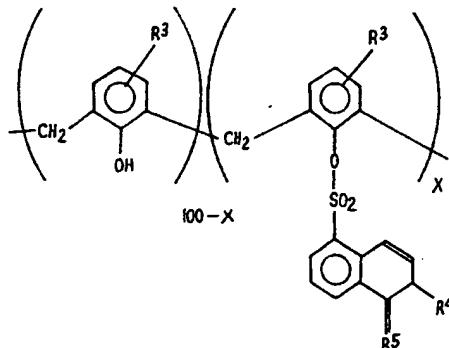
wherein R is H, an alkyl group having 1 to 3 carbon atoms, an alkoxy group having 1 to 3 carbon atoms or a cyano, halo or nitro group and m is an integer from 0 to 4, and which has a boiling point equal to or less than 200°C at atmospheric pressure; and

10 C a coating solvent.
 2. A composition according to claim 1, m in said formula being 0, 1 or 2.
 3. A composition according to claim 1 or 2 wherein the volatile carboxylic acid is present in a concentration range of from 1 to 50% by weight based on the total
 15 solids weight of said composition.
 4. A composition according to any of Claims 1 to 3 comprising also a non-light sensitive film-forming polymer wherein the weight ratio of light sensitive polymer to non-light sensitive polymer is in the range of from 1:1 to 99:1.
 5. A composition according to Claim 4 wherein the non-light sensitive polymer
 20 has been formed by the addition polymerization of one or more unsaturated compounds containing the group $>\text{C}=\text{C}<$.
 6. A composition according to any of the preceding Claims wherein the quinone diazide group is linked to the phenol-aldehyde resin through a linking group selected from sulphonyl



linkages.

7. A composition according to any of Claims 1 to 5, said light-sensitive polymer compound having the formula:



30 wherein R³ is H or methyl; R⁴ and R⁵ are interchangeably N₂ or O, and wherein R⁴ and R⁵ are not the same; and X is from 1 to 99 mole percent.

8. A composition according to Claim 1 substantially as described in any Example from 1 to 4 herein.

35 9. A photosensitive element which comprises a support bearing a layer of a photosensitive composition which has been formed by coating a composition of any claim from 1 to 8 on a support and evaporating the volatile carboxylic acid and any solvent therefrom.

10. A photosensitive element according to Claim 9 in which said support is an anodised aluminium support.

40 11. A photosensitive element according to Claim 9 which has been made substantially in accordance with Example 5 herein.

12. A process for preparing a photomechanical image which comprises imagewise exposing a photosensitive element according to any of Claims 9 to 11 and developing the element with an alkaline solution.

L. A. TRANGMAR, B.Sc., C.P.A.,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1979.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.